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Free Energy of Mixing of Melts in Mn_2SiO_4 - Fe_2SiO_4 System[†]

Nobuya IWAMOTO* and Hideaki SUIITO**

Abstract

The free energy of mixing of Mn_2SiO_4 - Fe_2SiO_4 has been determined from the phase diagram calculation. It was found that a maximum deviation from Ideal Silicate Mixing of approximately -3.8 KJ. per mole of orthosilicate ($\text{MO} \cdot \frac{1}{2} \text{SiO}_2$). Richardson model of ideal silicate mixing has been discussed at the composition of orthosilicate.

1. Introduction

Despite the importance of a knowledge of the thermodynamics of mixing in silicate melts to the understanding of high temperature processes, there exists a general lack of direct experimental data on such systems. Solution models, therefore, are of practical value in permitting extrapolation of scanty data and estimation of mixing properties. In addition, examination of the applicability of such models helps to further, although indirectly, our insight into the ionic constitution of melts at high temperature processes.

Only one structurally based model exists which permits the calculation of the properties of a ternary silicate from a knowledge of the properties of the constituent binaries; this is the Richardson model of ideal silicate mixing.⁽¹⁾ Masson's recent polymerization model^(2,3), which has been found to be reasonably successful in describing the behavior of binary silicates, has not yet been extended to ternary systems. The Richardson model assumes that the free energy of mixing two binary silicates of the same metal oxide: silica ratio is ideal, i. e., the additional free energy arises solely from the entropy of randomly mixing the cations in a constant silicate anion matrix. At the metasilicate composition and for mole fractions of silica above about 0.42 the model has been reasonably successful. However, with the apparent exception of the MnO - FeO - SiO_2 system⁽⁴⁾, significant deviations have been observed at the orthosilicate composition.^(1,5,6)

2. Previous Work

The equilibrium between molten iron and slags containing FeO , MnO , MgO and SiO_2 have been

studied using both MgO crucibles and SiO_2 crucibles by Bell⁽⁴⁾. The equilibrium constant for the reaction between molten iron containing manganese and slag;



is represented by

$$K_{\text{Mn}} = \frac{\gamma_{\text{MnO}} N_{\text{MnO}}}{\gamma_{\text{FeO}} N_{\text{FeO}} (\% \text{Mn})} = \frac{\gamma_{\text{MnO}}}{\gamma_{\text{FeO}}} K'_{\text{Mn}} = 3.5 \quad (1)$$

From the theory of ideal mixing of silicates, we obtain the following relation (APPENDIX)

$$\frac{\gamma_{\text{MnO}}}{\gamma_{\text{FeO}}} = \frac{a_{\text{MnO } b_1}}{a_{\text{FeO } b_2}} \times \sqrt{\frac{a_{\text{SiO}_2 } b_1}{a_{\text{SiO}_2 } b_2}} \quad (2)$$

where b_1 , b_2 denote the binary systems MnO - SiO_2 , FeO - SiO_2 respectively and x denotes $x\text{MnO} \cdot \text{SiO}_2$.

This is a constant for any given silica content and is independent of $N_{\text{MnO}}/N_{\text{FeO}}$ ratio. If ideal mixing of silicates occurs in the systems FeO - MnO - SiO_2 and FeO - MnO - MgO - SiO_2 , it will be seen from eq. (1) and (2) that K'_{Mn} will be a function only of N_{SiO_2} . It has been shown by Bell⁽⁴⁾ that no significant variation of K'_{Mn} with FeO/MnO ratio at a given silica content was found and that the ratio K_{Mn} was found to increase with increasing silica content of the slags. $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ can be calculated from eq. (2) by using the data on the binary systems FeO - SiO_2 , and MnO - SiO_2 . The variation of the ratio K'_{Mn} calculated with silica content ($0 < N_{\text{SiO}_2} < 0.35$) is in good agreement with the experimental data for the FeO - MnO - MgO - SiO_2 system. Bell concluded that ideal mixing of silicate occurs in the FeO - MnO - SiO_2 and FeO - MnO - MgO - SiO_2 systems.

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3. Calculation of Free Energy of Mixing in the $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ - $\text{MnO} \cdot \frac{1}{2} \text{SiO}_2$ System

A detailed experimental investigation of the orthosilicate part of the system was made by Carter, Murad and Hay⁷⁾. The diagram obtained in their study is shown in **Fig. 1**. For the system $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ - $\text{MnO} \cdot \frac{1}{2} \text{SiO}_2$, the partial molar free energy of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ in the liquid phase and in the solid phase is equal

$$\bar{G}_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (l)} = \bar{G}_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (s)} \quad (3)$$

By choosing the pure liquid and the pure solid component at any temperature T as the standard state of component in the liquid and solid mixtures, respectively, eq. (3) may be written as

$$\Delta G_f^\circ = \Delta H_f^\circ \text{FeO} \cdot \frac{1}{2} \text{SiO}_2 \left(\frac{T_f - T}{T_f} \right) = RT \ln \frac{a_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (s)}}{a_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (l)}} \quad (4)$$

where ΔG_f° ; free energy of fusion of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$

ΔH_f° ; heat of fusion $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$

T_f ; melting point of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$

$$\ln a_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (l)} = \frac{\Delta H_f^\circ}{R} \cdot \frac{T - T_f}{T T_f} + \ln a_{\text{FeO} \cdot \frac{1}{2} \text{SiO}_2 (s)} \quad (5)$$

It has been shown by the recent work of Schwerdtfeger and Muan⁸⁾ that the solid solution in the system at 1150°C behaves ideally within limits of experimental errors. Consequently, activity of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ is equal to mole fraction of cations along the pseudobinary phase diagram for this system. The resulting activities of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ along the liquidus may be calculated from eq. (5), using the heat of fusion of iron orthosilicate (46.1 KJ. per mole of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$)⁹⁾ and melting point of iron orthosilicate (1483°K). Neglecting the temperature dependence, appropriate Gibbs-Duhem integration gives the activity of $\text{MnO} \cdot \frac{1}{2} \text{SiO}_2$. This is shown in **Fig. 2**. The integral free energy of mixing shown in **Fig. 3** shows a maximum deviation

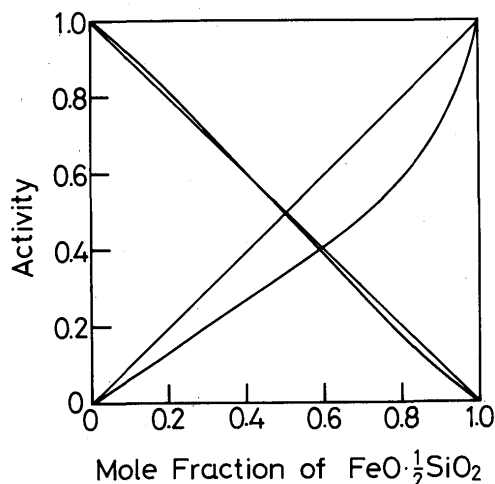


Fig. 2. Calculated activity of $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ along the liquidus in the $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ - $\text{MnO} \cdot \frac{1}{2} \text{SiO}_2$ system. Based on the work of Schwerdtfeger and Muan,⁸⁾ and Riboud and Muan.⁹⁾

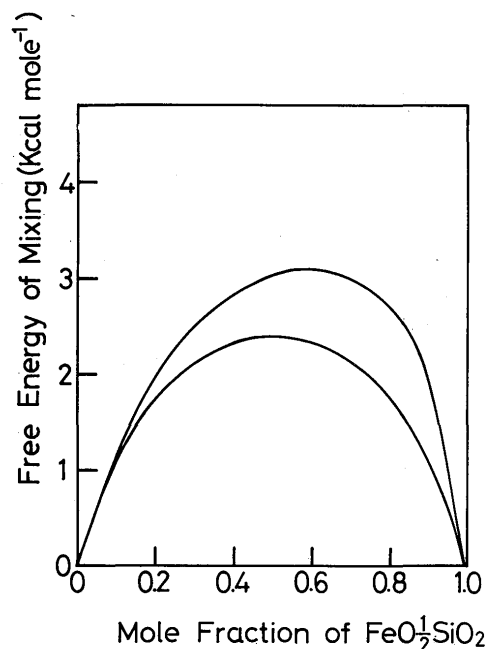


Fig. 3. Free energy of mixing per mole of liquid orthosilicate ($\text{MO} \cdot \frac{1}{2} \text{SiO}_2$).

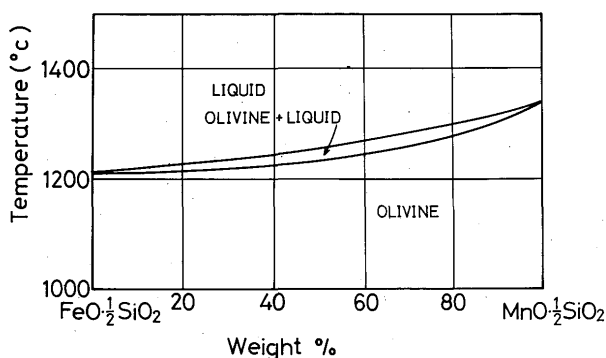


Fig. 1. Diagram illustrating phase relations in the system $\text{FeO} \cdot \frac{1}{2} \text{SiO}_2$ - $\text{MnO} \cdot \frac{1}{2} \text{SiO}_2$ (after Carter, Murad, and Hay.⁹⁾).

of approximately -3.8 KJ. per mole of $\text{MO} \cdot \frac{1}{2} \text{SiO}_2$ from ideal silicate mixing.

Since Bell's study⁴⁾ involved melts which were saturated with magnesia (the mole fraction of MgO ranging as high as 0.42) the above approximate value is to be preferred for the maximum deviation from ideal silicate mixing. Thus the weight of evidence is that, so far, there is no liquid system which obeys the ideal silicate mixing model in detail at the orthosilicate composition. Deviation from ideal silicate mixing from previous studies of liquid orthosilicate systems are given in **Table 1**.

Table I. Deviations from Ideal Silicate Mixing from Previous Studies of Liquid Orthosilicate Systems.

System	Temp °C	Max. deviation kJ. per mole MO. $\frac{1}{2}$ SiO_2	Method	Ref.
$\text{Mn}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$	1550	≈ 0	From measurements of the partitioning of O and Mn between liquid Fe and MgO-saturated melts	4
$\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$	1550	- 1.4	Estimated from the phase diagram	1
$\text{Ca}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$	1660	- 12	From measurements of Mn distribution between solid Pt and the melts	5
$\text{Ca}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$	1150	- 14	From phase diagram calculations using demonstrated ideal mixing in the solid solutions	6
	1600	- 15	Using a_{FeO} data for CaO-FeO- SiO_2 slags	
$\text{Ca}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$	1670	- 15	Estimated from the phase diagram	6

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APPENDIX

If ideal mixing holds in the MnO-FeO-SiO_2 system

$$a_{(\text{xMnOSiO}_2)} = \frac{a_{\text{MnO t}}^x a_{\text{SiO}_2 \text{ t}}}{a_{\text{MnO b}_1}^x a_{\text{SiO}_2 \text{ b}_1}} = N_{(\text{xMnOSiO}_2)}^x$$

$$\frac{a_{\text{MnO t}} a_{\text{SiO}_2 \text{ t}}^{\frac{1}{x}}}{a_{\text{MnO b}_1} a_{\text{SiO}_2 \text{ b}_1}^{\frac{1}{x}}} = N_{(\text{xMnOSiO}_2)} = N'_{\text{Mn}}$$

where N' is the cation fraction

$$a_{\text{MnO t}} = a_{\text{MnO b}_1} N_{\text{Mn}}' \times \sqrt{\frac{a_{\text{SiO}_2 \text{ b}_1}}{a_{\text{SiO}_2 \text{ t}}}}$$

Similarly

$$a_{\text{FeO t}} = a_{\text{FeO b}_2} N_{\text{Fe}}' \times \sqrt{\frac{a_{\text{SiO}_2 \text{ b}_2}}{a_{\text{SiO}_2 \text{ t}}}}$$

$$\frac{a_{\text{MnO t}}}{a_{\text{FeO t}}} = \frac{a_{\text{MnO b}_1}}{a_{\text{FeO b}_2}} \frac{N_{\text{MnO t}}}{N_{\text{FeO t}}} \times \sqrt{\frac{a_{\text{SiO}_2 \text{ b}_1}}{a_{\text{SiO}_2 \text{ b}_2}}}$$

$$\frac{\gamma_{\text{MnO}}}{\gamma_{\text{FeO}}} = \frac{a_{\text{MnO b}_1}}{a_{\text{FeO b}_2}} \times \sqrt{\frac{a_{\text{SiO}_2 \text{ b}_1}}{a_{\text{SiO}_2 \text{ b}_2}}}$$

where suffix t denotes the activity of the component in the ternary system.